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HIGH PRESSURE COSMOCHEMISTRY APPLIED TO MAJOR PLANETARY INTERIORS: EXPERIMENTAL STUDIES

Investigators

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SUMMARY

The overall objective of this project is to determine the properties and boundaries of several high pressure phases of the H_2-He-H_2O-NH_3-CH_4 system that are needed to constrain theoretical models of the interiors of the major planets. This is one of the first attempts to measure phase equilibria in binary fluid solid systems in diamond anvil cells and, in that respect, represents an attempt to advance the state of modern high-pressure experimentation. Vibrational spectroscopy of materials confined in externally heated cells is our primary experimental probe, The spectroscopy is supplemented by direct visual observation and x-ray diffraction crystallography. We also are measuring adiabats of these materials which provide constraints for models of heat flow in these bodies.

Our initial efforts have focused on the NH_3-H_2O binary. This system is especially relevant to models for surface reconstruction of the icy moons of Jupiter and Saturn. It also is relatively easy to handle and helps us to identify technical problems with the proposed studies so that we can eliminate them or minimize their effects before we add the more volatile components. During the period covered by this report (11/82-4/83), we completed a study of the infrared spectra of H_2O ice VII and D_2O ice VII, developed techniques for measuring adiabats of phases of NH_3-H_2O to 5 GPa, and completed construction of a mixing system for pressurized fluids in which liquid solutions of definite compositions can be prepared and loaded reliably into diamond cells.

Detailed Description of Work in Progress During the Period 11/1/82-4/30/83
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Infrared Spectra of Ice VII

Professor Wilfried Holzapfel's interest in infrared spectra of aqueous ices and our desire to develop analytical procedures for high pressure phases of the CH_4-NH_3-H_2O "ices" motivated us to develop an infrared capability during his recent visit to UCLA. We were fortunate to be able to adapt one of our high pressure cells to Professor Kaesz's Nicollet FTIR spectrometer for this work so that the diamond cell could be easily interchanged for his more conventional sample holders. With this arrangement, Professor Holzapfel determined the effect of pressure on much of the infrared spectra of H_2O and D_2O ice VII at room temperature and pressures between 2 and 15 GPa. At all pressures, two librational modes, $\nu_R^1E_u$ and $\nu_R^2E_u$, one bending mode, $\nu_2A_{2u}^1$, and various overtone bands were well well resolved; however, resolution was poorer in the region of the O-H stretching modes, ν_1 and ν_3, as a result of absorption by the diamonds and the weakness of the source. Most features shifted to slightly higher frequencies with increasing pressure. However, two species show more unusual behavior ($\nu_R E_u$ increases rapidly while ν_1 and ν_3 slowly decrease with pressure) which indicate that the O-H-O bond becomes symmetric at high pressures. These results are described in detail in the accompanying preprint which has been submitted for inclusion in the proceedings of Lunar and Planetary Science XIV.

As a result of this effort, we can now routinely use infrared as well as Raman spectroscopy to characterize high pressure phases of the "ices". However, the strength of the infrared bands of these systems means that thin samples must be used, and it is difficult to do surveys with such samples. The the present arrangement also permits us to measure FTIR spectra only at room temperature; however, we can easily construct a variable-temperature sample holder should the need arise.

Adiabats of H_2O-NH_3 Solutions at High Pressures

For several years, Dr. Reinhart Boehler of UCLA's Institute of Geophysics and Planetary Physics has measured adiabats, $(dT/dP)_S = \alpha VT/Cp$, of solids of physical (the highly compressible alkali metals) and geophysical (quartz, MgO) interest to pressures of the order of 5 GPa. These adiabats are the relevant equations of state for convecting planets, while the pressure dependences of the adiabats and the thermal expansivity, α, can be used to derive the Gruneisen parameters needed to convert shock Hugoniots to isotherms. Discussion between Dr. Boehler and Professor Nicol about methods to protect the alkali metals, rubidium and cesium, from attack by the surrounding hydrostatic pressure medium lead to a solution which should be generally applicable to compressible condensed phases of reactive materials. The method involves filling a thin bellows of an appropriate metal with the material without creating a vapor bubble.

After success with cesium, we decide to try to encapsulate liquid H_2O and a saturated (approximately 30%) aqueous solution of NH_3 and to measure adiabats for these samples to 3 GPa at room temperature. Fig. 1 shows the data obtained for these samples including the unusual rise of $(dT/dP)_S$ for liquid water below 0.7 GPa, the dramatic discontinuities at the liquid-ice VI and ice VI-VII boundaries, and the relatively high precision of the measurements. The solution data show the more typical decrease of $(dT/dP)_S$ with compression of the fluid phase and a change of slope near 2.4 GPa where ice separates from the fluid. We are now preparing bellows for other NH_3-H_2O samples including many with vapor pressures greater than 1 bar near room temperatures. During Summer 1983, Ms. Schwake will measure adiabats for these samples at room and higher temperatures. We also anticipate redesigning the piston-cylider apparatus used for these experiments so that some measurements can be made at lower temperatures.

Phase Diagram of $NH_3 \cdot H_2O$

Our previous reports have described our preliminary surveys of the NH_3-H_2O phase diagram and our conclusion that the compositions of the samples prepared by partial crystallization of the relevant solids at low temperatures varied to an unacceptable degree because of included solution, incomplete phase separation, and other factors. We further determined that Raman spectroscopy alone was insufficiently to determine the precise composition of the samples. Much of our work since then has been related to development of techniques for loading samples of known compositions.

During the Fall, Ms. Schwake tested a sample handling system in which precisely weighed amounts of liquid water and compressed ammonia could be mixed as a cold , atmospheric-pressure fluid of known concentration which could be loaded directly into the high pressure cell. Although this system solved the precision problem, it proved very difficult to manipulate; more than 80% of Ms. Schwake's attempts to load samples by this method ended in failure. Thus, Ms. Schwake and Dr. Johnson decided to replace this glass and metal system with an all-metal system in which the fluid could be mixed and the cell loaded at room temperature under elevated pressure. The all-metal system was completed during March and immediately proved to be satisfactory. Work on the phase equilibria has now resumed.

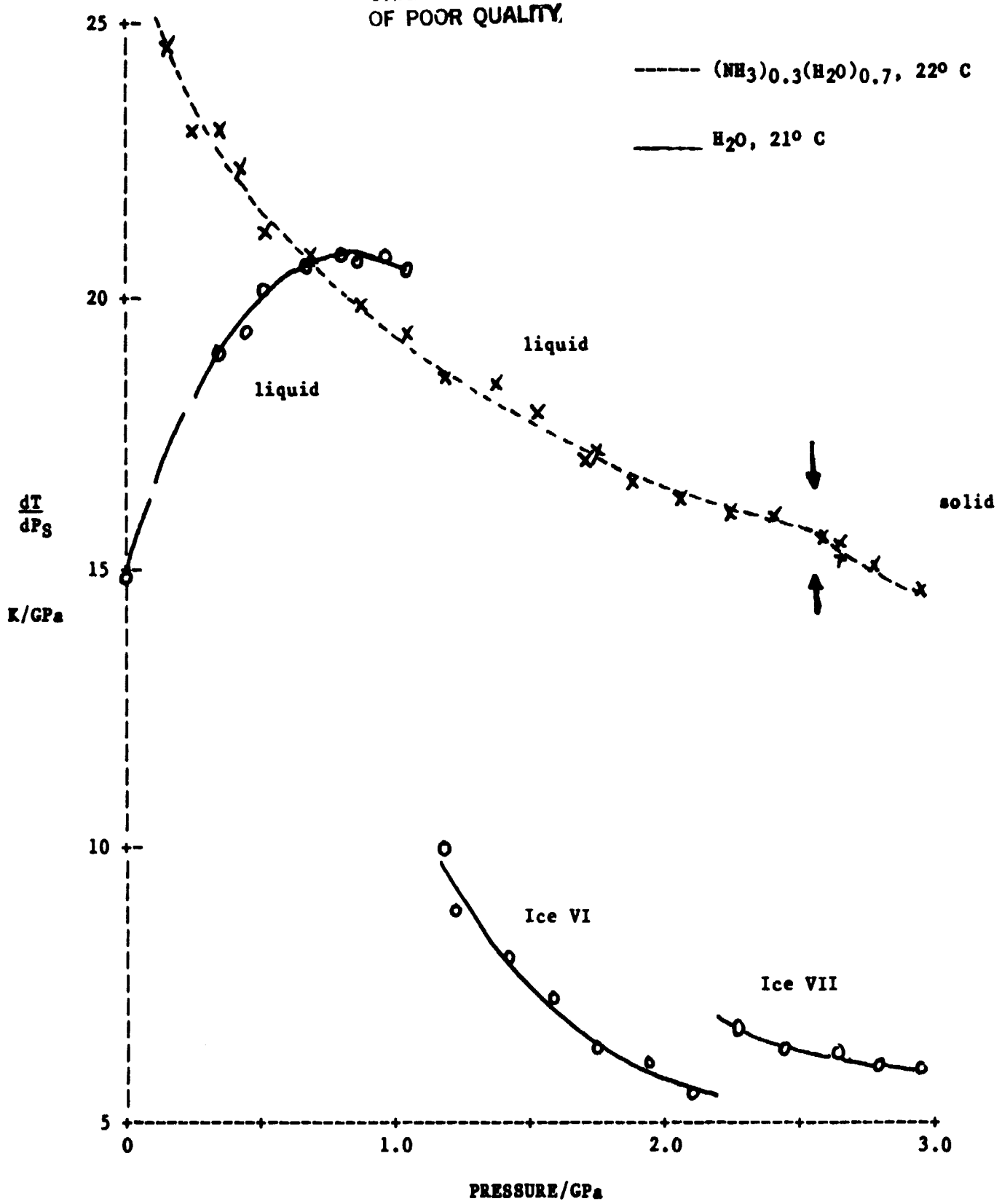

Fig. 1. Adiabats of H_2O and $(NH_3)_{0.3}(H_2O)_{0.7}$ near 295 K

Personnel

Most of the development, testing, and experimental work during the first two years of this grant were performed under Professor Nicol's direction by Ms. Andrea Schwake, a postgraduate associate who was trained in high pressure technology by Professor Holzapfel. In September 1982, Ms. Schwake resigned her full-time position to pursue a doctoral program in the Department of Chemistry and Biochemistry. She continued to work on the NH_3-H_2O studies on a half-time basis during the Fall Quarter. However, during the Winter and Spring, Andrea had to devote most of her time to course work, service as a teaching assistant (required as part of the doctoral program), and cumulative examinations, although she has helped out as much as these graduate student duties permitted. During the Summer, Andrea will resume regular participation in this project and will be involved with the adiabats.

In mid-January, Dr. Mary Johnson, joined the research group. Her initial tasks were to improve the reliability of the techniques Andrea had developed and to extend spectroscopic and phase equilibria studies to compositions and components other than 1:1 H_2O-NH_3. Mary is now in the midst of data collection.

Three other senior associates also contributed to this work. The infrared studies of H_2O and D_2O were obtained by Drs. Wilfried Holzapfel (a visiting professor on leave from the University of Paderborn) and B. Seiler (a postdoctoral fellow in Professor Kaesz's group). Dr. Reinhart Boehler, an Assistant Research Geophysicist in UCLA's Institute of Geophysics and Planetary Physics, measured the adiabats of ammonia-water solutions.

Bibliographic Data

W.B. Holzapfel, B. Seiler, and M. Nicol, "Effect of Pressure on Infrared Spectra of Ice VII", Lunar and Planetary Science XIV (Lunar and Planetary Institute, Houston, 1983), pp 321-2. (Abstract)

W.B. Holzapfel, B. Seiler, and M. Nicol, "Effect of Pressure on Infrared Spectra of Ice VII", (submitted to J. Geophys. Res.). (Preprint appended)